THE EXTRACTION OF ZINC FROM CERTAIN RETORT RESIDUES BY WET METHODS

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY WILLIAM PHILLIP UDINSKI

ENTITLED THE EXTRACTION OF ZINC FROM CERTAIN RETORT RESIDUES BY WET METHODS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

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II INTRODUCTION

1. Remarks on the metallurgy of zinc

The metallurgy of zinc, though perhaps the least efficient metallurgical process widely used, has in the last 200 years, undergone less change than that of any other metal. This is true in spite of the large increase in the usefulness of zinc both in quantity and in manner.

An inquiry concerning the efficiency of the smelting process as conducted in a typical American plant shows that only about 86% of the zinc is actually recovered in good practice. Much of the loss is in zinc held back in the retort residues.

Were it not for the sulfuric acid made as a by-product, the cost of zinc would be quite prohibitive for most of its ordinary applications. An undoubted saving could be accomplished were it possible to extract cheaply the last of the zinc remaining in these residues. Such an attempt is the object of this work.

2. Object of this work

In order to determine more definitely the condition and amount of zinc retained in these residues, and to study the possible means of recovery, investigation has been made of residues from a typical zinc smelter, using a fairly standard smelting practice on a high grade Joplin blende ore.

3. Survey of the literature

The literature since 1881 offers not a single detailed

exposition of work done on zinc extraction from such residues, although a few papers have been published dealing with the recovery of precious metals and of coal. During the same time, however, half a dozen patents were granted in this country and in Europe on various methods for recovering zinc.

The first one mentioned was granted in England to Fry[1] in 1898. It advocated stirring with a green pole the carbonaceous residues mixed with raw ore, on a basic hearth.

Homel's[2] British patent in 1907 was about the same as Fry's, omitting the green pole, but specifying the subsequent treatment of the fume with sulfur dioxide solution, the precipitation as a monosulfid by heating the $ZnH_2(SO_3)_2$ formed and final ignition to ZnO.

Stolzenwald's[3] United States patent 1908, is similar to Homel's, but omits the treatment of the fume.

MacIvor[4] in 1906 was granted an English patent for treating the residues with calcium chloride and sulfuric acid to obtain a solution of zinc chlorid.

Stolzenwald's[5] German patent 1908 suggested concentrating the residues by screening and blowing.

The last one mentioned is a United States patent to Jones[6] in 1914. The zinc is to be concentrated by igniting the pile of residues at the bottom. The volatilized zinc product will

1. Journal of Soc. Chem. Ind., v. 18, 281
2. Chem. Abs. 1908, 2212
3. Chem. Abs. 1909, 229
4. Chem. Abs. 1908, 335
5. Chem. Abs. 1908, 1546
6. Chem. Abs. 1914, 3774

condense in the cooler portion at the top of the pile. The concentrate can then be treated as an ordinary ore.

Where the residue carries values in precious metals, it[7,8] has been mixed in small quantities after sintering with regular lead charges.

4. Material worked on

The material worked on was the residue from the distillation of a roasted Joplin blende ore concentrate smelted at a large plant in central Illinois. The concentrate was roasted for sulfur dioxide and the product which still contained some sulfate was mixed with anthracite coal and distilled in a Belgian type of zinc furnace. It is evident that any sulfate remaining in the roasted ore would be reduced during the distillation process to sulfide and would remain in the retort residues. This would account for a part at least of the zinc in the residues.

5. Obtaining the sample

At the plant in question, the residues cleaned from the retorts had been stored in a large pile awaiting the time when they might be profitably treated for recovery of the zinc and coal which they contained. The sample used in this work was taken by scooping up at random, about ten kilograms of the material from the edge of the pile, without any effort at obtaining a completely representative sample.

7. Johnson, Met. and Chem. Eng. v. 18, 135
8. Stock, Met. and Chem. Eng. v. 19, 275

6. Analysis for fineness

The residue as received gave the following tests for fineness on a 2400 gram portion:

TABLE I

Fineness Analysis Of The Residues

Size of mesh	%
On 10	41.7
Thru 10 on 40	43.3
Thru 40	15.0

7. Interpretation of analytical results

All the results of the analyses which are given in this paper must be interpreted carefully. Care was taken to use a representative portion, for analysis, of the amount of residues available for experiment. The amount thus available, however, was not strictly a fair sample of the pile from which it was taken and was still less typical of the total by-product of the zinc furnaces of that plant. That aside however, an effort was made to secure each result as accurate as circumstances permitted. The author feels that even the roughest determination, that is for fineness, is not in error over one per-cent and that the others are as much more accurate than this as they are proportionately more important.

III THE EXTRACTION OF THE ZINC

1. Idea of the work

The idea adopted in this work was to extract the zinc and iron content of the residues with a solvent. From this extract the zinc was to be removed either as the metal or in the form of a salt. It was decided that the first attempt would be to electrolyze the solution for the metal, because this seemed the most profitable course. The first step was to determine the effect of the commonest solvents on the residues and then pick out the one which seemed most suitable, for electrolytic experiments.

2. Definition of "critical strength"

The critical strength of reagent may be defined as that concentration which contains just sufficient active material (Cl^-, OH^-, SO_4^{--}) in a given volume to combine with all the zinc and iron in the weight of rèsidues which the given volume of reagent will cover. In the absence of other limiting factors the critical strength of reagent was considered the best to start with in each case. With sulfuric acid it was thought advisable to experiment also with acid of approximate density 1.55 as this is about the strength of chamber acid.

3. Method of extracting

The extraction was made by covering the residues with sufficient reagent and allowing the mixture to stand for ten days. It was then filtered and the residues washed, until the washings gave no reaction with $K_4Fe(CN)_6$. The resulting solution was concentrated to a known volume and analyzed for

zinc and iron.

4. Results of extraction

Table 2 following, gives the results obtained with HCl and H_2SO_4 on the sample in various degrees of fineness.

TABLE II

Zinc Extracted By Hydrochloric Acid and Sulfuric Acid

Sample Marked	Reagent	Fineness	% Iron Extracted	% Zinc Extracted	Remarks
8a	HCl 1.057	As del'vd	27.60	45.30	Critical Strength
8b	" "	" "	30.70	50.20	" "
8c	" "	" "	30.30	46.10	" "
Average			29.53	47.20	
8e	H_2SO_4 1.131	" "	33.80	39.70	" "
8f	" "	" "	33.20	38.90	" "
8g	" "	" "	36.50	38.92	" "
8h	" "	" "	22.20	35.25	" "
Average			31.60	38.19	
9a	HCl 1.057	95 + % through 100 mesh	65.40	50.80	" "
9b	" "		60.00		" "
9c	" "		88.00	46.20	" "
9d	" "		73.90	49.00	" "
Average			71.80	48.30	
9e	H_2SO_4 1.137	95 + % through 100 mesh	72.30	43.10	" "
9f	" "		76.50	45.20	" "
9g	" "		77.50	46.90	" "
Average			75.43	45.10	
10e	H_2SO_4 1.557	95 + % through 100 mesh	80.20	56.20	App. Chamber Acid
10g	" "		74.80	61.00	" "
10h	" "		78.00	61.00	" "
Average			77.70	59.40	
11e	H_2SO_4 1.557	As del'vd	33.30	48.40	" "
11f	" "	" "	34.80	53.00	" "
11g	" "	" "	35.00	61.90	" "
11h	" "	" "		65.20	" "
Average			34.50	57.10	

SUMMARY

Reagent	Density	Fineness	% Iron Extracted	% Zinc Extracted	Remarks
HCl	1.057	As dl'vd	29.53	47.20	Critical Strength
H_2SO_4	1.131	" "	31.60	38.19	" "
H_2SO_4	1.557	" "	34.50	57.10	App. Chamber Acid
HCl	1.057	95 %	71.80	48.30	Critical Strength
H_2SO_4	1.137	through	75.40	45.10	" "
H_2SO_4	1.557	100 mesh	77.70	59.40	App. Chamber Acid

5. Conclusions from Table II

Several conclusions may be drawn from these tables:

(1) Only about 60% of the zinc is soluble in sulfuric acid. This is possibly due to zinc ferrite formed during the roasting and the distillation. This compound according to Ingalls[1] is insoluble in H_2SO_4. Isherwood[2] advocates further treatment with heat and pressure. Vigorous agitation during the period of extraction would very likely increase the amount of zinc recovered.

(2) In the leaching of zinc with H_2SO_4 the important factor is the degree of fineness of the material rather than the strength of acid. In the case of iron the contrary is true.

6. Distribution of zinc as to fineness

An attempt was made to ascertain the distribution of the extractable zinc and iron among the different degrees of fineness of the material. For this purpose the sample as delivered was divided into three parts, the first that which remained on 10 mesh, the second that which passed through 10 mesh but remained on 40 and the third that which passed through 40. The results obtained are given in Table III. It should be

1. Ingalls, Met. and Chem. Eng. v. 14, 264
2. Isherwood, British Patent 2285

explained that the percentage figures refer to one total portion; thus for the sample marked 1a under the heading "percent by weight of total portion" is given the figure 34.5. This means that the sample marked 1a weighed 34.5% of the total sample marked a, which was divided according to fineness into three portions each marked 1a, 2a and 7a, respectively. The same remark applies to the figures given under the headings "percent zinc and percent iron extracted".

TABLE III

Distribution Of Extractable Zinc And Iron As To Fineness

Sample Marked	Reagent	Fineness	% By Weight Of Total Sample	% Iron Extracted On Total Sample	% Zinc Extracted On Total Sample	Remarks
1f	H_2SO_4 1.137	On 10	43.50	10.90	18.30	Critical Strength
1g	" "	"	36.20	8.50	18.60	
1h	" "	"	36.80	12.15	14.00	
Average			38.50	10.52	15.63	
2f	" "	Through 10 On 40	47.00	63.00	56.00	
2g	" "	"	53.80	65.60	56.00	
2h	" "	"	45.10	66.20	55.50	
Average			48.63	64.93	55.83	
7f	" "	Thru 40	10.00	27.10	27.70	
7g	" "	"	10.00	24.90	27.40	
7h	" "	"	17.60	21.75	30.50	
Average			12.53	24.58	28.53	
1a	HCl 1.057	On 10	34.50	11.10	24.40	
1c	" "	"	35.10	13.90	17.50	
1d	" "	"	38.60	14.70	20.00	
Average			36.07	13.23	20.63	
2a	" "	Thru 10 On 40	48.30	58.50	44.80	
2c	" "	"	49.80	56.00	48.60	
2d	" "	"	46.20	53.70	45.70	
Average			48.10	56.07	46.37	

(Continued)

(Table III Concluded)

Sample Marked	Reagent	Fineness	% By Weight Of Total Sample	% Iron Extracted On Total Sample	% Zinc Extracted On Total Sample	Remarks
7a	HCl 1.057	Thru 40	17.20	30.40	30.30	"
7c	" "	"	15.10	30.10	33.90	Critical
7d	" "	"	15.20	31.60	34.30	Strength
Average			15.83	30.70	35.80	"

SUMMARY

Reagent and Density	Fineness	% By Weight Of Total Sample	% Iron Extracted On Total Sample	% Zinc Extracted On Total Sample
HCl 1.057	On 10	36.07	13.23	20.63
" "	Thru 10 On 40	48.10	56.07	46.37
" "	Through 40	15.83	30.70	35.80
H_2SO_4 1.137	On 10	38.50	10.52	15.63
" "	Thru 10 On 40	48.63	64.93	55.83
" "	Through 40	12.53	24.58	28.53

7. Conclusions from Table III

The results given in Table III are somewhat erratic. We may, however, safely draw the conclusion that about 80% of the extractable zinc and iron is contained in the 60% of the residues that pass through a ten mesh sieve. The disproportion is not sufficiently great to be important.

IV ELECTROLYSIS OF ZINC

1. General considerations

The electrolysis of zinc was, as might be expected, first considered as a means for the rapid estimation of zinc. A number of methods have been outlined in the journals from time to time, most of them giving quite a quantitative separation. None of them, however, lends itself to extension on a scale suitable for the commercial extraction of zinc. The reasons are, the costly electrodes, the restrictions in the concentration of electrolyte, the large quantities of inorganic addition reagents, and in some cases the costliness of changing the zinc over to the particular compound advocated for electrolysis. In many cases, too, the process loses its advantages entirely when the layer of deposited zinc exceeds 0.1 or 0.2 mm. A commercially successful process on the other hand need not be quantitative, but must be economical and must yield a satisfactory deposit.

Unfortunately, the electrolysis of zinc sulfate offers much greater difficulty than that of the corresponding copper salt. It must also be remembered that in the case of copper the successful process is the purification of an almost pure material present as a soluble anode, whereas, in this work we aim to electrolyze the zinc from a steadily diminishing concentration of electrolyte.

2. Important factors in electrolysis

The important factors in the electrolytic process may be listed as follows in the order in which they usually have

to be considered:

(1) The nature of the anion.

(2) The concentration of the zinc ion.

(3) Impurities in the electrolyte.

(4) Addition reagents.

(5) Zinc sponge.

(6) Electrodes.

(7) Circulation of the electrolyte.

(8) Current density, current efficiency, voltage efficiency, and energy efficiency.

(9) Minor factors, temperature, etc.

3. Nature of the anion

About half a dozen different inorganic anions have been suggested. SO_4^{--} is easily the favorite, Cl^- may be placed next. Others worthy of mention are CN^- in $K_2Zn(CN)_4$[1]; $(OH)^-$ from Na_2ZnO_2; $(OH)^-$ from $Zn(NH_3)_4(OH)_2$ in a solution containing NH_4Cl; HSO_3^-[2]; F^-[3] as ZnF_2 in a solution containing NH_4F; and the fluosilicate[4] ion in a zinc fluosilicate solution.

In this country for commercial processes SO_4^{--} is probably used exclusively. In Europe the Hoepfner process[5] using $ZnCl_2$ and the Sanna[6] process using $Zn(NH_3)_4(OH)_2$ have found application. The objections that may be raised against $ZnCl_2$ are the special electrodes necessary and the complicated system

1. Moore, Chem. News, v.53, 209
2. Lossizza, French Patent 370803
3. Mätuschek, German Patent 244930
4. Goldschmidt, Chem. Abs. 1909, 1621
5. Gunther, Darstellung des Zinks, pp. 99-180
6. Sanna, Eng. and Mining Journal, v. 89, 1106

of circulation of electrolyte, and against $Zn(NH_3)_4(OH)_2$ the invariable deposition of spongy zinc. To the advantage of the $ZnCl_2$ is the production of Cl. To that of $Zn(NH_3)_4(OH)_2$ is the non-solution from the original material of most of the troublesome impurities. It also has a lower decomposition potential than either $ZnSO_4$ or $ZnCl_2$ with the consequent advantage in the consumption of energy. On the other hand, the SO_4^{--}-ion has the advantage of economy in that sulfuric acid weight for weight of active material is by far the cheapest and most readily available of the three reagents. In its favor also is the satisfactory deposit which may be obtained from the sulfate solution under proper conditions. Hansen[1] thinks the hydrate process to be impossible while Sanna[2] considers it superior to any other in his knowledge. Snowdon[3] concludes from his investigation that either acid or alkaline solutions may be used.

4. Concentration of the zinc ion

The concentration of the zinc ion is very important. It varies in different cases from saturation[4] with respect to the particular zinc salt used to 2 percent[5] for $ZnSO_4$. Gruner[5] gives 5% $ZnSO_4$ and 5% acid as the most favorable concentration for maximum current efficiency while for the energy consumption a minimum concentration should be 10%. Increasing the acid

1. Hansen, Met. and Chem. Eng., v. 14, 120
2. Sanna, Eng. and Min. Jour., v. 89, 1106
3. Snowdon, Trans. Am. Elec. Chem. Soc., v. 11, 121
4. Paweck, French Patent 336773
5. Gruner, Chem. Abs. 1916, p. 3033

content lowers the rate of precipitation but also decreases the drop of potential. On the other hand, increasing the zinc content increases the size of the crystals deposited[1]. A few patents have been granted on specific electrolyte concentrations. A German patent to Bianco[2] specifies $ZnSO_4$ 125-375; $FeSO_4$ 6-40; $Al_2(SO_4)_3$ 3-63; $NaC_2H_3O_2$ 2-3; H_2O 864-487. Presumably this is to be used for coating iron with a layer of zinc. Another to Kern[3] calls for $ZnCl_2$ 10; Na_3AlCl_6 6-5; NaCl 2; beet sugar 3-4; H_2O 100. A British patent to Tainton[4] requires $ZnSO_4$ 10-11%; acid 10-30%; gum tragacanth 0.1-1%. The most favorable concentration very likely varies considerably with circumstances.

5. Acid concentration

The concentration of the acid is under best conditions very low[5]. Satisfactory deposits are obtainable, however, with acid concentrations as high as 30% according to Gruner[6]. Pring and Tainton[5] state that high acidity causes a fall in efficiency.

6. Impurities in the electrolyte

The most troublesome impurities obtained in the extraction of ores are copper and arsenic. These are, however, absent in our solution, the only impurity being iron. This must always be removed. When the iron content is high it is deposited to the exclusion of zinc. Up to the concentrations of about 1% Pring and Tainton[5] conclude that the iron is not

1. Snowdon, Trans. Am. Elec. Chem. Soc. v. 11, 121
2. Bianco, German Patent, 241170
3. Kern, German Patent 244432; U. S. Patent 999568
4. Tainton, British Patent 7235
5. Pring and Tainton, J. C. S. v.105, 710
6. Gruner, Chem. Abs. 1916, 3033

deposited in its due proportion. Thus solutions containing 0.1 to 1% of iron gave deposits with only 0.05 to 0.1%. The zinc concentration was around 10%. The authors, however, do not show what theoretical results based on the Nernst formulae were to be expected, so this conclusion is in doubt. Holbrook[1] gives even more surprising results. He states that a solution containing 20 grams $ZnSO_4$ and 50 grams $FeSO_4$ per liter gave a deposit with only 6.21% iron, while another solution containing 3o grams of each per liter yielded a deposit with only 1.25% iron. To remove the iron, it must be oxidized to the ferric state and precipitated with an alkali. MnO_2 is the oxidizing agent most often used and the precipitating agent may be ZnO[2] or powdered limestone[3]. Buddeus[4] advocates the following procedure: The ferrous iron and zinc are precipitated with $CaCO_3$ or Na_2CO_3, the precipitate filtered, washed, and dried, thus converting the iron to the fèrric state. From the dried mixture the zinc may be leached out. Holland and Bertiaux[5] recommend addition of H_2SO_3 to the sulfate solution followed by neutralization with NaOH and addition of KCN. $K_4Fe(CN)_6$ is formed and from this only zinc is deposited.

7. Addition reagents

By the term addition reagent is meant a substance added to the solution in order to improve the deposit, or the

1. Holbrook, Thesis Univ. of Wisconsin, 1912
2. Siemans and Halske, German Patent 213004
3. Ingalls, Met. and Chem. Eng., v. 14, 264
4. Buddeus, U. S. Patent 1120683
5. Holland and Bertiaux, Compt. Rend., v. 136, 1266

efficiency of the process. Organic addition agent are usually used in small amounts to improve the deposit, but it has also been shown that certain inorganic salts have a favorable effect without at the same time decreasing the energy efficiency as is invariably the case with organic materials. Oxalate ions[1]; Na_2SO_4; Na_2SO_4 plus $Na_2C_2H_3O_2$ plus glacial acetic acid[2]; NH_4Cl plus Na_2SO_4[3]; $(NH_4)_2SO_4$[4]; and $MnSO_4$[5] (French process), are recommended by different men. Inorganic agents may sometimes have to be added in amounts comparable to the concentration of the zinc in solution. In many cases organic matter will be present in the solution due to its being extracted in small amounts from the ore, so that it is not necessary to add any further quantity. Watts and Shape[6] investigated fourty-two different reagents in a solution containing 25% $ZnSO_4 \cdot 7H_2O$, at 22° C., using a current density of 1.2 amp./sq.dm., and addition reagent in the proportion of 1 gram per liter. They concluded that beta-naphthol was the best reagent to use. Pring[7] favors gum arabic. Resorcinol has also been recommended. Pring and Tainton[8] found the addition of 0.5 gram gum arabic and 0.5 gram dextrin to be most advantageous in their work. The same authors in their paper give a discussion on the theories proposed concerning the part played by colloids

1. Reinhardt, J. A. C. S., v. 24, 193
2. Price, Chem. News, v. 97, 89
3. Lemetere, British Patent 11432
4. Wilson and al., U. S. Patent 1083785
5. Lyon and al., Met. and Chem. Eng., v. 14, 30
6. Watts and Shape, Trans. Am. Elec. Chem. Soc., v. 25, 291
7. Pring, comment on 6 above.
8. Pring and Tainton, J. C. S., v. 105, 710

in electrolysis.

8. Spongy zinc

Spongy zinc deposits have not greatly troubled in American practice. It is, however, the general type of deposit from hydrate solutions. Sanna,[1] the leading exponent of the hydrate process, claims to be able to compact the zinc sponge by subjecting it to heat and pressure simultaneously. Pring and Tainton[2] cite several theories proposed concerning the formation of this deposit. According to these authors Mylius and Fromm[3] attribute the formation of porous zinc to the production of oxide, and action which is increased by presence of oxidizing agents and diminished by reducing agents or in acid solutions. Apparently the contrary opinion is held by Siemens and Halske[4] who think the porous zinc to be due to the formation of zinc hydride, and that, therefore, its formation is hindered by oxidizing agents or chlorine which oxidize the hydrogen. A later investigation by Forester and Gunther[5] leads these workers to the conclusion that the production of zinc sponge is due to the following phenomena. In an acid solution, the solution may become at the cathode locally alkaline. Under this condition the deposited zinc is energetically oxidized by atmospheric oxygen with the formation of ZnO. "It is finally shown in detail that all definitely

1. Sanna, Eng. and Min. Jour., v. 39, 1106
2. Pring and Tainton, J. C. S., v. 105, 710
3. Mylius and Fromm, Zeit. Anorg. Chem., v. 9, 158
4. Siemens and Halske, Dingl. Poly. Tech. Jour. 1893, 258
5. Forester and Gunther, Electrochemie v. 5, 13

ascertained facts relating to the formation of spongy zinc point to the conclusion that it is produced whenever the condition of the solution at the cathode is such that basic zinc salts or zinc hydroxide separate there."

9. Electrodes

The choice of electrodes is limited to such material as will add no complications to the electrolysis. In the case where the process is used for winning the zinc an insoluble anode must therefore be used. For commercial anodes lead is most often used, a notable instance being at Anaconda.[1] Fabricated PbO_2[2] has also been suggested. For cathodes Zn, Al[1], fabricated PbO_2[2], and Hg[3] (presumably for the high hydrogen overvoltage) have been advocated by different workers.

10. Circulation of electrolyte

The electrolyte is in all cases circulated or what amounts to almost the same thing in many cases the cathode is rotated. Information concerning the speed of rotation is vague as this is always expressed in r.p.m. without further description of the electrode. From the point of view of the electrolysis, there can be no maximum speed while the minimum speed probably varies widely with the conditions existing in each case. Snowdon[4] concludes on this point that the higher the rate of of circulation the higher the limiting current density above which the deposit becomes unsatisfactory.

1. Ingalls, Met. and Chem. Eng., v. 14, 264
2. Siemens and Halske, German Patent 195033
3. Reed, U. S. Patent 1200025
4. Snowdon, Trans. Am. Elec. Chem. Soc., v. 11, 121

11. Current Density

Low current densities are favored in commercial processes. It must be remembered that the heating effect varies as the square of the current. Nevertheless, Kern[1] in his patent specifies "a high current density". Tainton[2] calls for 0.11 to 0.55 amp./sq.cm. Snowdon[3] investigated the deposition of zinc at different current densities from 0.05 to 0.7 amp./sq.cm. He found that the best current density varied with the rate of circulation and the temperature of the electrolyte, also that increasing the current density decreased the size of the deposited crystals. Pring and Tainton[4] made an investigation bearing particularly on the "Electrodeposition of Zinc at High Current Densities". They cite in their paper the recommendations of a few authors on this point. Thus Mylius and Fromm[5] give about 0.15 amp./sq.cm. as the best current density for very slightly acid solutions of $ZnSO_4$. Killiani[6] obtained good results with densities varying from 1.8-10 amp./sq.cm. In their own investigations the authors (Pring and Tainton) used values from 3-10 amp./sq.cm. They concluded that other things being equal, increasing the current increases the tendency of the deposit to tree, but up to 0.5-0.6 amp./sq.cm. it also increases the efficiency. In another place Pring[7]

1. Kern, German Patent 244432
2. Tainton, British Patent 7235
3. Snowdon, Trans. Am. Elec. Chem. Soc., v. 11, 121
4. Pring and Tainton, J. C. S., v. 105, 710
5. Mylius and Fromm, Zeit. Anorg. Chem., v. 9, 153
6. Killiani, Berg. und Huttenman Zeit., 1883, 251
7. Pring, Comment on Watts and Shape Trans. Am. Elec. Chem. Soc., v. 25, 291

advocates densities of 0.5-0.6 amp./sq.cm. Ingalls[1], describing the process at Anaconda mentions current densities at the cathode of 0.022-0.033 amp./sq.cm. The average being about 0.025 amp./sq.cm.

12. Temperature

The temperature of the solution has considerable influence on the various phases of the electrolytic process. For best results it should be low. In a patent Lemetre[2] specifies "below 30° C." Snowdon[3] finds that the maximum current density for satisfactory deposit goes down with increasing temperature, furthermore, increasing the temperature increases the size of the crystals deposited. The latter effect is borne out by the investigations of Pring and Tainton[4].

13. Reasons for choice of the sulfate solution in this work

Sulfuric acid was chosen as the most suitable for electrolysis of the reagents used. The reasons for this are several: (1) The zinc smelter usually manufactures this acid (2) It is cheaper than any of the others (3) But little more of H_2SO_4 (100% by weight) is required per pound of zinc, than its most likely competitor HCl (4) The sulfate solution gives the best promise of success in electrolysis.

As has been shown, however, the extraction of the zinc by H_2SO_4 is not nearly complete even with acid of density 1.55 and the residues in a condition so fine that 95 + % pass through a

1. Ingalls, Met. and Chem. Eng., v. 14, 264
2. Lemetre, British Patent 11432
3. Snowdon, Trans. Am. Elec. Chem. Soc., v. 11, 121
4. Pring and Tainton, J. C. S., v. 105, 710

100 mesh sieve. It was, therefore, not considered worth while to go into great detail in the matter of electrolysis, but rather to determine in a general way the behavior of such an extract as might be expected in actual practice. For this purpose the residues as received were covered with H_2SO_4 of about 1.5 times critical strength and allowed to stand for ten days, then filtered and washed. The solution was concentrated until the volume was about twice that of the original reagent added, then after several refiltrations it was considered ready for electrolysis. It may be added here that difficulty was encountered in freeing the solution from SiO_2. After the solution was apparently free from solids, it would again deposit particles of precipitate on standing for a short time. After refiltering the same thing would happen and the final solution obtained after four filtrations still precipitated SiO_2 on standing.

14. Solutions used for electrolysis

The three solutions listed below were used in electrolysis:

Solution I. Zinc 0.06 gm./cu.cm. (about 15% $ZnSO_4$). Iron 0.0198 gm./cu.cm. (about 6% $FeSO_4$). Acidity 1.0 N (about 10% acid). Silica and organic matter in undetermined amounts. Probably very small amounts of the other metals present in the residues (see qualitative analysis). Remarks: This solution was obtained as described above.

Solution II. Zinc 0.04 gm./cu.cm. (about 9% $ZnSO_4$). Iron - trace. Acid - trace. Other metals as in solution I. Silica and organic matter. Ammonium sulfate in undetermined

amount (perhaps 10-15%). Remarks: This solution was made by neutralizing solution I with NH_4OH, oxidizing the iron with bromine and precipitating as $Fe(OH)_3$ with NH_4OH. For some reason a very small portion of the $Fe(OH)_3$ remained suspended in the colloidal state and could not be filtered out. Due to this cause the solution II contained a trace of iron.

Solution III. Zinc 0.03 gm./cu.cm. (about 8% $ZnSO_4$). Iron trace. Acid - close to 5%. Silica, organic matter, other metals and $(NH_4)_2SO_4$ as in solution II. Remarks: Made from solution II by addition of 5% of its volume of concentrated H_2SO_4.

15. Electrolytic apparatus

A 400 cu. cm. portion of these solutions was electrolyzed in the apparatus shown in Figure I below:

The Electrolytic Apparatus

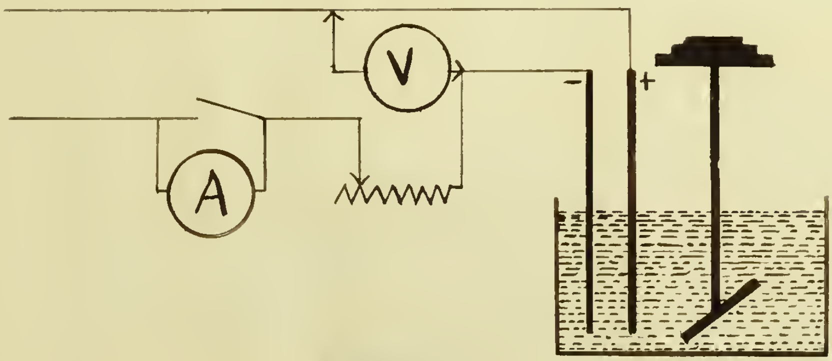
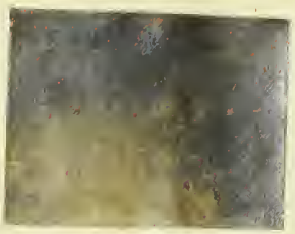


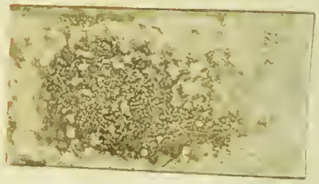
FIGURE I

This apparatus is defective in the matter of circulation of electrolyte, the tendency being rather to form local than to cause uniform circulation about the electrodes.

(To face page 23)



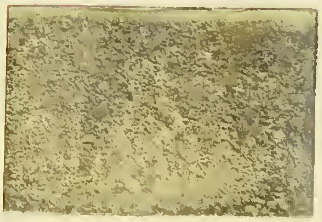
Cathode I



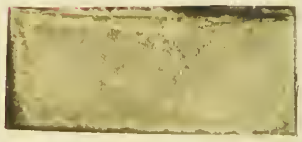
Cathode 6

Cathode 7

Cathode 8



Cathode 9



Cathode IO

Cathode II

Photographs of Cathodes in Table VI

16. Results of eletrclysis

In Table IV below are given the details and the results of the electrolysis and following that photographs of some of the electrodes mentioned in the table.

TABLE IV

Results Of The Electrolysis

No.	Sol'n.	Anode	Cathode	Anode Current Density Amp./sq.cm.	Cathode Current Density Amp./sq.cm.	Rev./min. Of stirrer
*1	I	Fe	Fe	0.152	0.216	560
2	I	Fe	Fe	0.390	0.315	560
3	I	Fe	Fe	0.500	0.546	560
4	I	Pb	Fe	0.170	0.180	560
5	I	Pb	Fe	0.180	0.200	560
*6	II	Pb	Al	0.150	0.130	560
*7	II	Pb	Al	0.130	0.150	560
*8	III	Pb	Al	0.170	0.180	560
*9	III	Pb	Al	0.150	0.170	560
*10	III	Pb	Fe	0.200	0.240	560
*11	III	Pb	Fe	1.200	2.400	560

No.	Sol'n.	Distance Between Electrodes In Cm.	Potential Gradient Volts/cm.	Remarks
*1	I	3.0	1.1	Cathode deposit on drying showed rusty spots, indicating the deposit of much iron. Anode went into solution.
2	I	2.5	1.5	
3	I	2.5	2.0	
4	I	2.2	1.6	Zinc deposit coarsely granular and loose.
5	I	1.9	1.9	Addition agent 1 gm. $MnSO_4$. No appreciable advantage over No. 4.
*6	II	2.5	2.0	Zinc deposit, dark, granular and loose.
*7	II	2.5	2.2	Addition agent 1 gm. $MnSO_4$. Deposit dark, coarsely granular, but adherent. Ran only 5 min.

(continued)

(Table IV concluded)

No.	Sol'n.	Distance Between Electrodes In Cm.	Potential Gradient Volts/cm.	Remarks
*8	III	2.4	1.7	Addition agent 1 gm. $MnSO_4$. Deposit light and smooth. Ran only 10 minutes.
*9	III	3.0	2.8	Addition agent naphtalene. Deposit coarse, but adherent.
*10	III	2.4	3.1	Cathode deposit fair, but poor at edges.
*11	III	2.7	6.7	Cathode deposit dark, but smooth and adherent.

* Photographs of these cathodes are shown herewith.

17. Conclusions on the elctrolysis of zinc solutions used

Any electrolytic process may be must changed by slight variation in any one of its various phases. It is thus a risky matter to reason about it. Especially is this true where the results are obtained with so simplified an apparatus as was used in these experiments. We can therefore only say that the results point in general to certain probably conclusions:

(1) The solution obtained by extraction will not give a good deposit without the removal of the iron.

(2) The solution containing 5% of acid gives a better deposit than the barely acid solution.

(3) The addition of naphtalene is of doubtful value.

(4) The addition of $MnSO_4$ is of some advantage at least if the deposition is not continued too long.

(5) The use of the solution with the iron removed for zinc plating on iron does not appear advisable because of the coarseness of the deposit and its tendency to be loose.

V CONCLUSIONS

1. The probable economy of the process

The economy of the process for obtaining zinc from retort residues after the manner of this experiment is doubtful. In the first place the sulfuric acid does not completely extract all the zinc and in the second place, the satisfactory recovery of the zinc from the extract is difficult to accomplish.

2. Other possible methods

The work described above by no means exhausts the possible methods of extracting the zinc. Let us remember that these residues are comparatively free from metals other than zinc and iron and that they are very readily available for treatment. Let us further remember that sulfuric acid is a relatively cheap commodity to the zinc smelter and that the extraction of the zinc was made with very simple apparatus. It may be that some one of the salts of zinc are sufficiently valuable to justify the extraction of the zinc in the form of that salt, the acid for this leaching being made, if possible, at the smelter from the sulfuric acid there produced.

VI ANALYSIS OF THE RESIDUES

1. General remarks on the analysis

The residues in general, offer no special difficulty in their analysis either qualitatively on the whole list of cations or quantitatively for zinc and iron. Such difficulties as are involved are due to the presence of organic matter which has been dissolved out.

2. Preparation of the solution

The preparation of the solution is the same for the qualitative and the quantitative analyses. The residues are first ground to such fineness that at least 95 + % pass thru a 100 mesh sieve. The solvent is HCl assisted, it may be, by an oxidizing agent such as $KClO_3$ or HNO_3, care being taken to drive off all the chlorine or nitrogen oxides in each case. The resulting solution is several times taken down to dryness and redissolved in dilute HCl, to dehydrate the SiO_2 and remove part of the organic matter, extracted from the residues.

3. The qualitative analysis

The general procedure followed in the qualitative analysis is that outlined by W. A. Noyes in his "Textbook of Qualitative Analysis". Lead must be tested for separately, due to the fact that the above method involves the use of hot concentrated sulfuric acid in testing for this metal. The hot acid chars the organic matter and the solution turns black.

4. Results of the qualitative analysis

The qualitative analysis showed the following metals to

be present: Zn, Fe, Mg, Ca and Al (perhaps in very small amount); and the following to be absent: Pb, Cu, Cd, Cr, Mn, Co, Ni, Ba and Sr. Non-metallic constituents of the residues were: S, SiO_2, organic matter, anthracite coal and probably oxygen in metallic oxides.

5. The quantitative analysis

Quantitatively, the residues were analyzed for only zinc and iron. Information on the general quantitative estimation of the important constituents of zinc retort residues is given by Evans[1]. Demorest[2] writes concerning the determination of zinc in ores, which method is also applicable to residues. Low[3] gives four methods and several modifications of the same, for the quantitative estimation of zinc in "ores, etc.". It is likely, however, that any standard method of zinc and iron analysis could be modified to give sufficiently accurate results.

6. Estimation of the zinc

For zinc it was found best to use the method given by Scott[4] for the determination of zinc in acid solution with standard $K_4Fe(CN)_6$, using 10% $UO(NO_3)_2$ as an outside indicator. This method requires the preliminary separation of the iron as there outlined. The same author gives a titration method for zinc in alkaline solution which does not require the separation of the iron. In this case, however, it was found very difficult

1. Evans, Mining Science, v. 63, 440
2. Demorest, J. I. E. C., v. 5, 302
3. Low, Technical Methods of Ore Analysis, 7th ed. pp.284-303
4. Scott, Standard Methods of Chemical Analysis, pp. 581

to determine the end point accurately.

7. Estimation of the iron

The iron was titrated with $KMnO_4$ after the addition of Zimmerman-Reinhardt reagent.

8. Results of the quantitative analysis for the zinc and iron

The results on three, five gram samples agreed remarkably well as the following table indicates:

TABLE V

Zinc And Iron In The Residues

Sample	% Iron	% Zinc
1	6.44	9.88
2	6.44	9.56
3	6.46	9.74
Average	6.45	9.73

9. Estimation of the combustible and the incombustible

The stimation of the combustible and of the residues remaining after combustion was done in this manner. The residue left after extracting the zinc and iron for quantitative analysis was dried, removed from the filter paper, the paper ignited and the ashes added to the dried residue. The weight of this represents the weight of combustible plus incombustible. The residue was then ignited over the blast to constant weight. From this could be calculated the weights of combustible and incombustible, respectively. It is to be admitted that this method cannot lead to very accurate results. Nevertheless, a little thought will suggest certain modifications which will

lead to better results. To compensate for the lack of accuracy in the individual determinations, six different samples were taken. It is hoped, thereby, a fairly representative average has been obtained. The results are given in the table below:

TABLE VI

Combustible and Incombustible in Residues

Sample	% Combustible plus Incombustible	% Combustible	% Incombustible
1	76.6	34.0	41.8
2	78.2	35.6	44.0
3	77.0	34.4	41.4
4	78.6	36.0	44.0
5	75.5	33.9	41.8
6	76.3	33.7	42.6
Average	77.2	34.6	42.6

The total of the averages of zinc, iron, combustible and incombustible contained in the residues is 93.38%. This leaves 6.62% unaccounted for. Most of this is probably magnesium and the rest is sulfur, oxygen and calcium.